Structural and Optical Characterization of Plasma Polymerized Pyrrole Monolayer Thin Films

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Abstract

Plasma Polymerized Pyrrole (PPPy) thin films of different thicknesses have been deposited onto glass substrates at room temperature by using a capacitively coupled parallel plate reactor. Fourier Transform Infrared (FTIR) and Ultraviolet-visible (UV-Vis) spectroscopy techniques have been used to characterize the as-grown thin films of about 400, 450 and 500 nm thickness. The structural analyses by means of FTIR spectroscopy have indicated that the monomer has undergone the re-organization and the ring structure has been retained during the plasma polymerization. From the UV-Vis absorption spectra, allowed direct transition (E_{qd}) and indirect transition (E_{qi}) energy gaps were determined. The E_{qd} for 400, 450 and 500 nm thick PPPy films were found to be 3.25, 3.47, and 3.58 eV respectively. On the other hand, the E_{qi} for the same series are 2.22, 2.25, and 2.35 eV respectively. From these results, it is seen that both the E_{qd} and E_{qi} are declined with the decrease in the thicknesses of the films, which is an indication of decreasing the resistivity of the film with lower thickness. This result would in turn cause an increase in electrical conductivity in the low-thickness thin film.

Keyword

Plasma Polymerization; PPPy Thin Film; FTIR; UV-Visible; Energy Band Gaps

Introduction

Plasma polymerization is a versatile technique for the deposition of thin films with different functional properties. Since they are formed with fragmented molecules under ions and electron collisions with high energy, the molecular structures of the films are different from starting materials [*Chowdhury* et al, 2000 and *Quan* et al, 2001] and suitable for a wide range of modern applications. Plasma polymerized films are usually found to be pinhole-free and highly cross-linked and therefore they are insoluble, thermally stable, chemically inert and mechanically tough. Furthermore, such films are often highly coherent and adherent to a variety of substrates including conventional polymer, glass and metal surfaces. Due to these excellent properties, they have been widely employed in the last few years for a variety of applications such as protective coatings, membranes, biomedical materials, electronic and optical devices, adhesion promoters, anticorrosive surfaces, humidity sensors, electrical resistors, scratch resistant coatings, optical filters, chemical barrier coatings, etc.

Various properties of the polymers such as structural, physical, chemical, optical and electrical properties have been investigated as appeared in literatures. The elemental compositions of plasma polymers produced from a variety of organic compounds using various kinds of plasma reactors was investigated [*Westwood*, 1971, *Yasud*a et al., 1976] and two major trends in the plasma polymers were reported namely: (i) the deficiency of hydrogen and halogens attached to the carbon in the monomers, and (ii) the incorporation of oxygen in the polymers even though the monomers exclude from oxygen. Based on these observations, they concluded that the incorporation of oxygen is a consequence of the post plasma reaction of trapped free radicals with ambient oxygen. The structural, optical and electrical characteristics of plasma polymerized pyrrole (PPPy) and iodine-doped PPPy prepared using an inductively coupled plasma reactor were studied [*Kumar et al*, 2003] and it was found that due to iodine doping the surface morphology of the PPPy film became smoother and an increase in the connectivity and continuity between the blocks of polymer chains provided an increase in conductivity.

Based on the FTIR spectra, they reported that the ring structure was retained during plasma polymerization and a chemical structure was also proposed for the PPPy film. The influence of electrode material and film thickness on charge transport properties of electrodeposited polypyrrole (PPy) thin films were studied [*Valaski* et al., 2001, 2002] and it was found that the morphology, roughness and electrical conductivity of the films are strongly influenced by the choice of substrate and the choice of electrode materials played a quite important role in specifying the resistivity as well as the conductivity [*Valaski* et al., 2001]. In the study on the influence of the film thickness [*Valaski* et al., 2002] on the conductivity, they found that different conduction mechanisms were shown by the films with different thickness. When film thickness was increased (~above 300nm) the charge transport tended to be space charge limited, but for smaller thickness ($d \leq 300$ nm) of the films, the charge transport was limited by thermoionic emission. The charge mobility was also found to be increased for the smaller thickness. It was also reported that the film morphology was highly thickness dependent. Different properties of plasma polymerized and iodine-doped polypyrrole have been investigated [*Rajan* et al., 2002]. A comparative study of the FTIR spectra of the monomer and polymer pyrrole gave information that the ring structure was retained during plasma polymerization.

This paper describes the preparation of plasma polymerized pyrrole (PPPy) monolayer thin films and discusses the chemical structure investigated by FTIR spectroscopy and optical properties of the thin films studied by UV-Vis spectroscopy. It is to be noted that the Optical Characterization [*Kamal* and *Bhuiyan*, 2011] and Direct Current Electrical Characterization [*Kamal* and *Bhuiyan*, 2012] of Plasma Polymerized Pyrrole-*N, N, 3, 5* tetramethylaniline bilayer thin films were carried out by Kamal and Bhuiyan. This paper aims to prepare and characterize the monolayer PPPy thin film from a different point of view, i.e., the unexpected changes in the physical properties with the change of the thickness of the thin films.

Experimental Details

Sample Preparation

A capacitively coupled parallel plate reactor has been used to deposit plasma polymerized pyrrole (PPPy) monolayer thin films with different thicknesses. The monomer pyrrole was collected from Aldrich-Chemie D-7924, Steinheim, England. The monomers vapour were introduced to the reactor through a flowmeter at the flow rate of about 20cm^3 (STP)/min into the glow discharge reactor. The glow discharge system, a bell-jar type capacitively coupled system, consisted of two parallel plate electrodes of stainless steel of diameter and thickness 0.09 and 0.001m respectively which were placed 0.035 m apart. The glow discharge chamber was evacuated by a rotary pump (Vacuubrand, Vacuubrand GMBH & Co, Germany) and plasma was generated around the substrates which were kept on the lower electrode, using a step up transformer connected to the electrodes with a power of about 30 W at line frequency. Transparent light yellow colored PPPy, monolayer thin films of different thickness were deposited onto the glass substrates. The deposition parameters such as flow-rate, deposition-time, power, vacuum order were kept almost same for all samples so that the comparison of the results could be made for various plasma polymerized samples. The thicknesses of deposited films were measured by a multiple-beam interferometric technique.

Fourier Transform Infrared (FTIR) Spectroscopy

For FTIR studies the as-grown PPPy monolayer thin film was scraped off from the glass substrates in powder form and mixed with potassium bromide (KBr) and then pelletized. These pellets of the mixture were used to record the FTIR spectra at room temperature using an FTIR spectrometer (Shimadzu -IR 470, Shimadzu Corporation, Tokyo, Japan). All the spectra were recorded in transmittance (%) mode in the wavenumber region 4000-500 cm-1.

Ultraviolet-visible (UV-Vis) Spectroscopy

UV-Vis spectra of grown PPPy thin films on glass substrates were obtained in absorption mode with a spectrophotometer Shimadzu UV-160A (Shimadzu Corporation, Tokyo, Japan) in the wavelength range from 200 to 800 nm at room temperature.

Results and Discussion

FTIR Spectroscopic Analyses

Fig. 1 represents the FTIR spectra of Pyrrole monomer and PPPy, and in the Table 1, the peak assignments for the pyrrole monomer and for the PPPy thin films are shown.

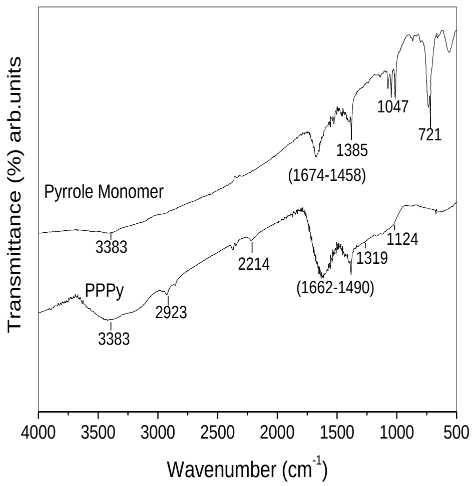

FIG.1 THE FTIR SPECTRA OF PYRROLE MONOMER AND PPPY

TABLE1. ASSIGNMENTS OF FTIR ABSORPTION PEAKS FOR PYRROLE MONOMER AND PPPY

Vibrations	Wavenumber (cm^{-1})	
	Pyrrole	PPPy
N-H stretching vibration of primary and secondary amines	3383	3383
Asymmetric and symmetric C-H stretching vibration of saturated hydrocarbon	-	2923
—N=C=O	-	2214
C=C conjugated and C=N conjugated stretch and N-H deformation vibration	1674-1458	1652-1490
Alkane C-H deformation	1384	-
C-N stretching vibration	1047	1124
Tetra substituted Benzene	-	-
C-H out of plane bending	721	-

In the FTIR spectrum of the pyrrole monomer and PPPy (Fig. 1), the absorption bands are found to be very close to those reported previously [*Eufinger* et al., 1996, *Rajan* et al., 2002 and *Kumar* et al., 2003]. It is seen that the FTIR spectrum of the PPPy is relatively complicated than that of the pyrrole monomer. Both spectra show a strong peak at about 3383 cm^{-1}, which is due to the N-H bond stretching vibration of primary and secondary amines and imines [*Eufinger* et al., 1996]. The absorption around 1650 cm^{-1} corresponds to the amines in the pyrrole structure. At about 2923 cm^{-1}, there is a sharp peak in PPPy spectrum but not in monomer spectrum. The peak is due to asymmetric and symmetric C-H stretching vibrations of saturated hydrocarbon. Pyrrole has highly strained ring so that the ring is easy to open under plasma polymerization. Therefore the FTIR spectrum of PPPy is very different to that of the monomer. In the molecular structure of the pyrrole monomer, all the carbon atoms are unsaturated. Thus, the peaks around 2900 cm^{-1} arise due to the plasma polymerization. There is another special peak around 720 cm^{-1} appears in the spectrum of pyrrole monomer, but not in the spectrum of PPPy. This peak usually belongs to $–CH_2–$ unites. All of these differences have indicated that the monomer undergone the re-organization during the plasma polymerization.

UV-Vis Spectroscopy

The variation of absorption (ABS) with wavelength, λ, for as grown plasma polymerized pyrrole (PPPy) thin films of different thicknesses of about 400, 450, 500, has been recorded from the UV-visible absorption spectra at room temperature and presented in Fig. 2. from which a bathochromic shift (a shift towards longer wavelength) of PPPy of about 20 nm is observed with respect to the pyrrole monomer, i.e., the peak values of PPPy (about 300 nm) have been shifted to higher wavelength compared to the peak wavelength (λ_{max}) value, 280 nm of the liquid monomer (inset of Fig. 2). It is well known that increasing conjugation generally moves the absorption to longer wavelength [*Gong* et al., 1998]. Therefore, this bathochromic shift (or red shift) in PPPy indicates the presence of an increased degree of conjugation in the resulting films. It is also seen from the figure that absorption peak intensity increases and broadens with increasing thickness of the films and a sharp rise of the absorption in the low wavelength side is observed. Then the absorption decreases rapidly up to about 400 nm with a peak at around 300 nm.

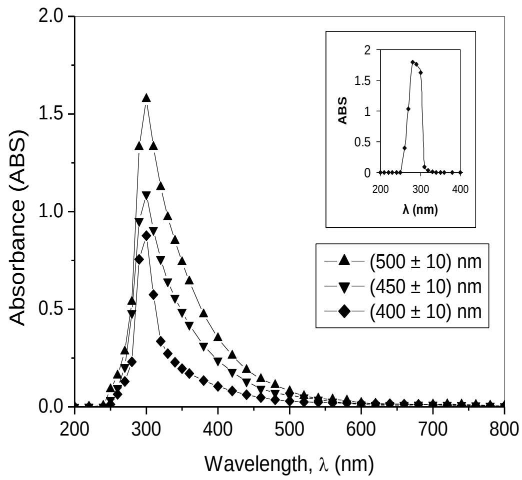

FIG. 2 VARIATION OF ABSORPTION (ABS) WITH WAVELENGTH FOR AS GROWN PPPY THIN FILMS OF THICKNESSES 400, 450 AND 500 NM (INSET: ABSORPTION FOR MONOMER PYRROLE)

The absorption co-efficient α was calculated from the absorbance data of Fig. 2 using the equation [*Al-Ani* et al., 1991]

$$\alpha = 2.303\left(\frac{A}{d}\right) \quad (1)$$

where *A* is the absorbance and *d* is the thickness of the thin film.

The spectral dependence of α as a function of energy hν for PPPy thin films with thicknesses 400, 450 and 500 nm is shown in Fig. 3. It is observed that in the low energy region the edges follow linear fall for values of α below about 5,000 cm^{-1} for all types of samples. These falling edges may either be due to lack of long-range order or due to the presence of defects in the thin films [*Mott* and *Davis*, 1971].

However, since α is used to describe the reduction in intensity of light in a medium as a function of distance, higher values of α is an indication of more reduction in intensity. From Fig. 3 it is observed that the thin films of lower thickness have higher values of the absorption co-efficient α, which indicates that in the films of lower thickness the intensity of light is reduced more.

The extinction co-efficient, k, can be computed from the absorption co-efficient α, using the following equation,

$$\alpha = \frac{4\pi k}{\lambda} \quad (2)$$

where λ is the wavelength.

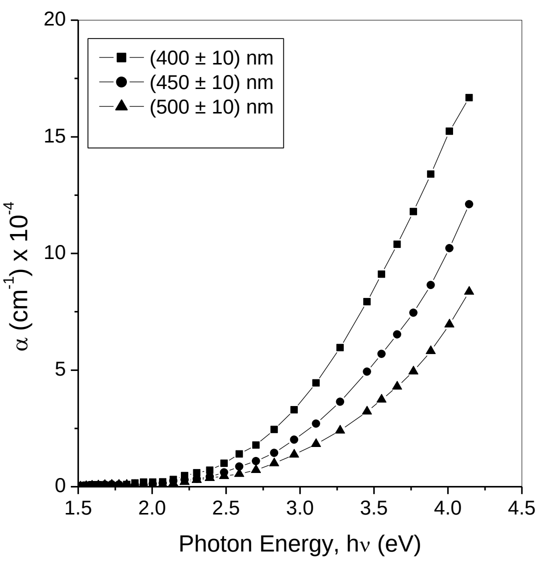

FIG .3 PLOTS OF ABSORPTION CO-EFFICIENT,α AS A FUNCTION OF PHOTON ENERGY, Hν, FOR AS GROWN PPPY THIN FILMS OF THICKNESSES ABOUT 400, 450 AND 500 NM

Fig. 4 shows the plots of extinction co-efficient, K, as a function of hν for grown PPPy thin films of thicknesses about 400, 450 and 500 nm.

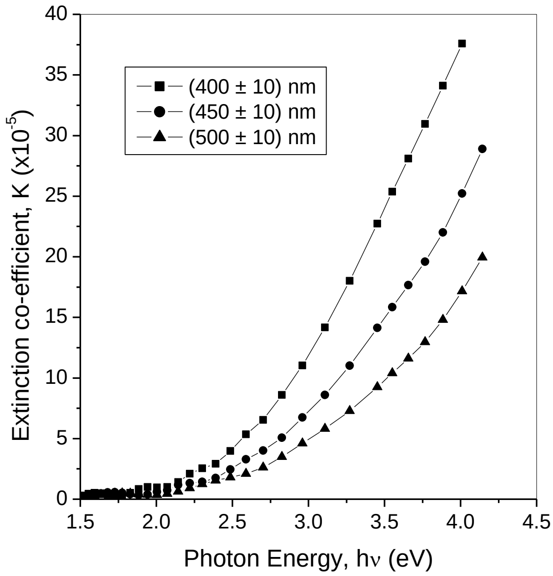

FIG. 4 PLOT OF EXTINCTION CO-EFFICIENT, K, AS A FUNCTION OF PHOTON ENERGY FOR PPPY THIN FILMS OF THICKNESSES ABOUT 400, 450 AND 500 NM

Since the extinction co-efficient describes the attenuation of light in a medium and the rise of K with the increase of hν indicates the probability of raising the electron transfers across the mobility gap with the photon energy, higher values of K are the representation of greater attenuation of light in a thin film and also the higher probability of raising the electron transfer across the mobility gap with the photon energy. In Fig. 4 it is seen that the film of lower thickness has higher value of K, which indicates that the light is more attenuated in the films of lower thicknesses than that of the films of higher thicknesses and the probability of raising the electron transfers across the mobility gap with the photon energy is higher in the films with lower thicknesses.

One of the most significant optical parameters related to the electronic structure is the optical band gap, E_{opt}, which can be calculated by Tauc relation [*Tauc*, 1974] given by equation (3), namely,

$$\alpha h\nu = B\left(E_{opt} - h\nu\right)^n \quad (3)$$

where *B* is the Tauc parameter, *n* is the parameter connected with distribution of the density of states and E_{opt} is the optical band gap obtained from the extrapolation of the linear part of the curve.

To indicate the presence of direct and indirect transitions in the PPPy thin films, the curves in Fig. 2

could be characterized with two different slopes. The allowed direct transition energy gap, E_{qd}, can be evaluated from the plots of $(\alpha h\nu)^2$ as a function of hν which is shown in Fig. 5, while the allowed indirect transition energy gap, E_{qi}, can be evaluated from $(\alpha h\nu)^{1/2}$ versus hν plots shown in Fig. 6. Both the energy gaps are determined from the intercept of the extrapolation of the curves to zero α in the photon energy axis. The values E_{qd} and E_{qi} obtained from the plots of Fig. 5 and Fig. 6 are documented in Table 2.

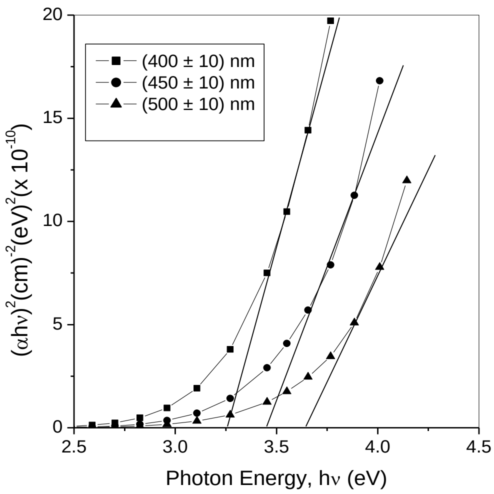

FIG. 5 $(\alpha H\nu)^2$ VERSUS Hν CURVES FOR AS GROWN PPPY THIN FILMS OF THICKNESSES ABOUT 400, 450 AND 500 NM

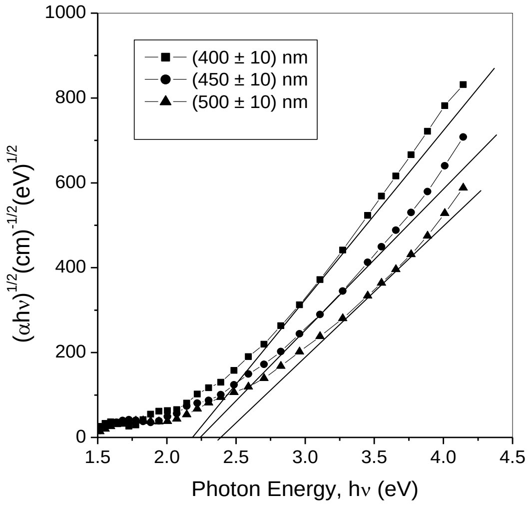

FIG. 6 (αHν)1/2 VERSUS Hν CURVES FOR AS GROWN PPPY THIN FILMS OF THICKNESSES ABOUT 400, 450 AND 500 NM.

It is seen from Table 2 that both the E_{qd} and E_{qi} are declined with the decrease of the thicknesses of the films, which is an indication of decreasing the resistivity of the film of lower thickness. This result would in turn cause an increase in electrical conductivity in the low-thickness thin film.

TABLE 2. THE ENERGY BAND GAPS OF PPPY THIN FILMS

Thickness of the films (nm)	Direct transition energy gap(eV) (E_{qd})	Indirect transition energy gap (eV) (E_{qi})
500	3.58	2.35
450	3.47	2.25
400	3.25	2.22

Conclusions

From the absorption spectra of PPPy monolayer thin films, it is observed that the absorption peak intensity increases and broadens with increasing thickness of all types of thin films, which is very expected result, since thicker materials usually absorb more radiation than thinner materials. A bathochromic shift (or a red shift) of PPPy of about 20 nm is observed with respect to the pyrrole monomer, which indicates the presence of an increased degree of conjugation in the resulting films.

From the study of dependence of α on hν, a general trend is observed that the thin films with lower thickness have higher values of the absorption coefficients α which indicate that in the films with lower thickness the intensity of light is reduced more. A similar trend is observed in the plots of extinction co-efficient, K, as a function of hν. It is seen that the film with lower thickness has higher value of K, which indicates that the light is more attenuated in the films with lower thicknesses than that of the films with higher thicknesses and the probability of raising the electron transfers across the mobility gap with the photon energy is higher in the films with lower thicknesses.

The most important result obtained from the optical characterization of PPPy monolayer thin films is about the band gaps of the films. It is observed that both the E_{qd} and E_{qi} are decreased with the fall of the thicknesses for all types of films, which is an indication of decreasing the resistivity of the film of lower thickness. This result would in turn cause an increase in electrical conductivity in the low-thickness thin film. The most probable reason of this behavior may be due to better morphological characteristics of the films with lower thickness. It has been reported [*Valaski* et al., 2002] that the film morphology is highly thickness dependent, and better morphology (lower roughness) has been observed for smaller thickness, which causes increased charge mobility. Moreover, the incorporation of oxygen is reported [*Yasuda* et al., 1976] as a typical phenomenon in the plasma polymerization, and in our study, the FTIR analyses of PPPy have also

indicated the presence of oxygen by the appearance of the absorption band at 2214 cm^{-1}. This oxidation of the films might affect the physical properties of the thin films, which might increase the resistivity of the films of higher thickness.

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Author's Biography

M. M. Kamal was born in 1970 in Dhaka, Bangladesh. He earned his Bachelor of Science (B. Sc) degree with honors and Masters of Science (M. Sc) degree in Physics from University of Dhaka, Bangladesh, in 1991 and 1992 respectively. In Master of Science he submitted a dissertation on the Theoretical Nuclear Physics for the partial fulfillment of the degree. In 2003 he earned his Masters of Philosophy (M. Phil) degree from Bangladesh University of Engineering and Technology (BUET) and submitted another dissertation on the Theoretical Crystal Growth. He was awarded the Doctor of Philosophy (PhD) from the same university in 2010 for his excellent creative research work on Plasma Polymer Thin films Characterization.

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research articles have been published in reputed international journals and a number of papers have been presented in different national and international conferences. His two recent publication are (i) "Optical Characterization of Plasma Polymerized Pyrrole-*N,N,3,5* Tetramethylaniline Bilayer Thin Films", published in Journal of Applied Polymer Science (Vol. 121, pp 2361 – 2368 , 2011) and (ii) "Direct Current Electrical Characterization of Plasma Polymerized Pyrrole-*N,N,3,5* Tetramethylaniline Bilayer Thin Films", published in Journal of Applied Polymer Sciences (Vol. 125, pp 1033-1040, 2012).

Dr. Kamal is a life member of Bangladesh Physical Society (BPS) and a very well known figure in many socio-cultural-scientific activities of his country.